A Rational Synthesis of Pt/C Catalysts

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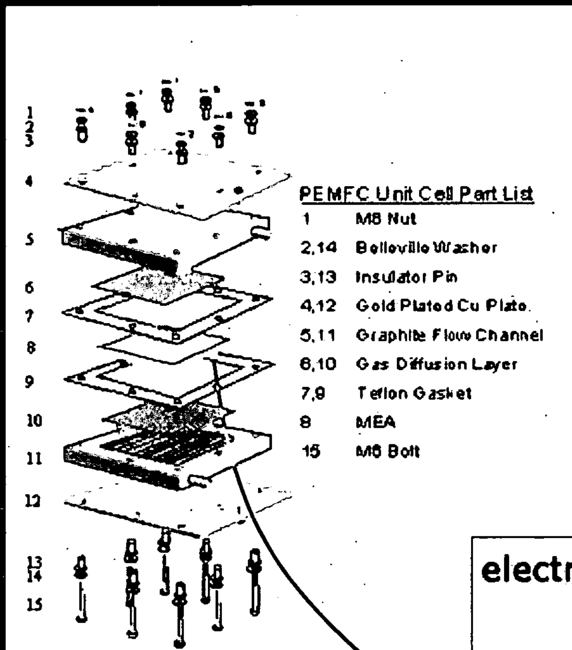
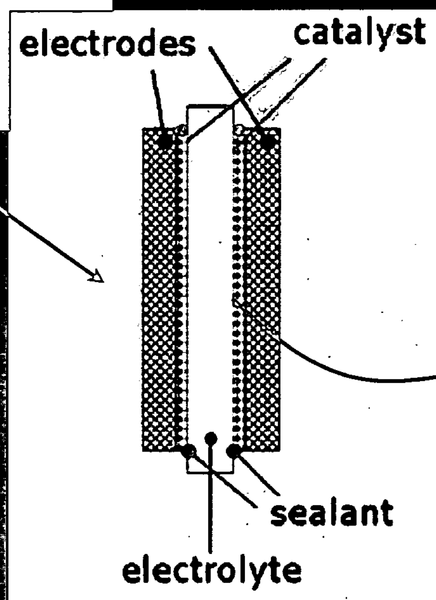
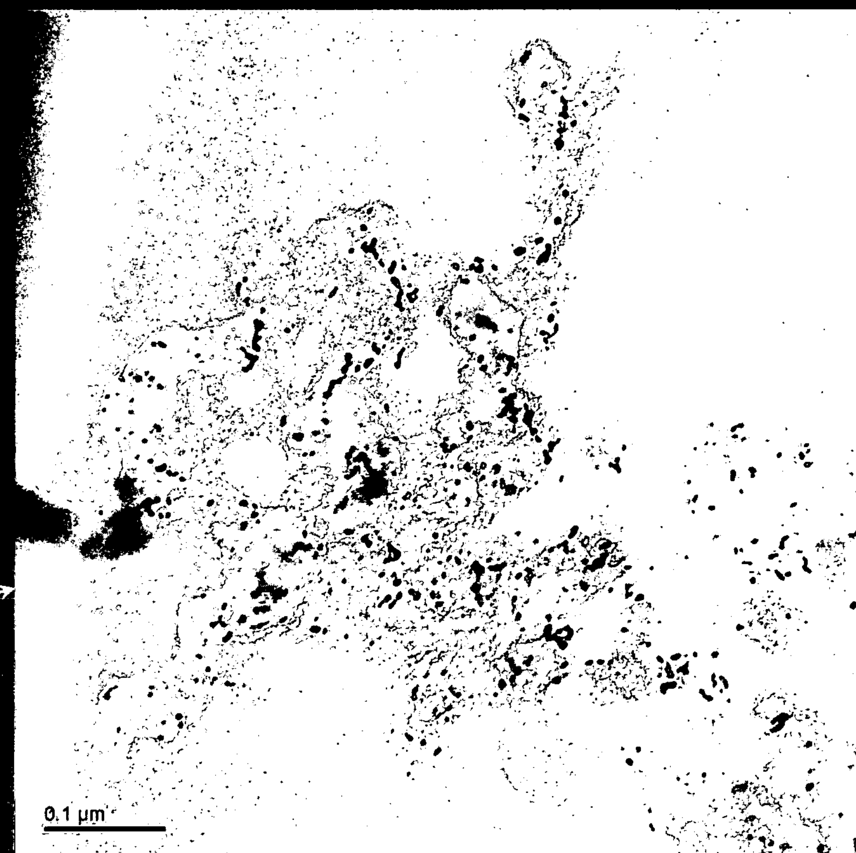
*Examples of catalyst synthesis presented here are examples and are not intended to limmit the invention.

Heart of a Fuel Cell

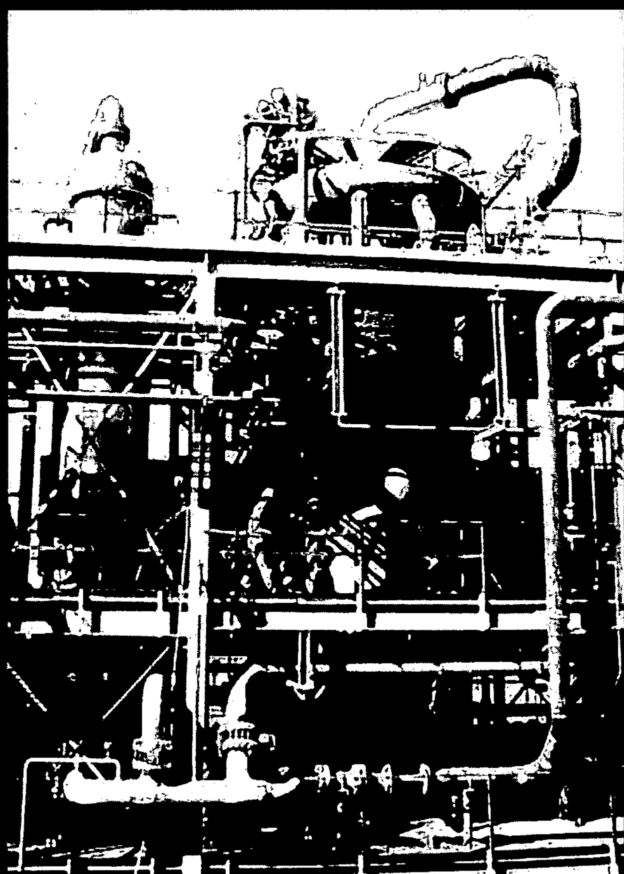


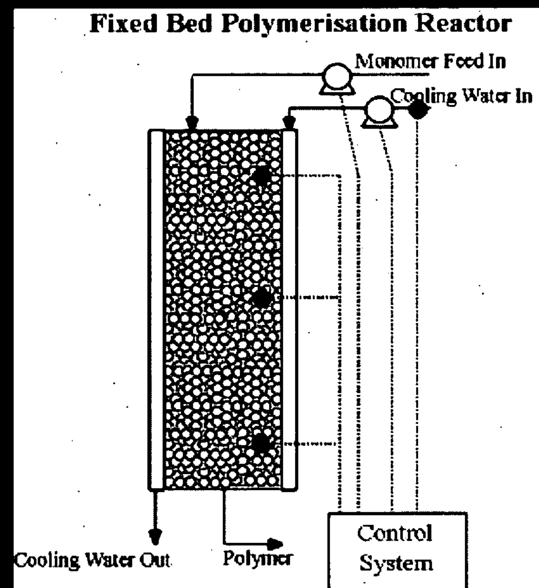


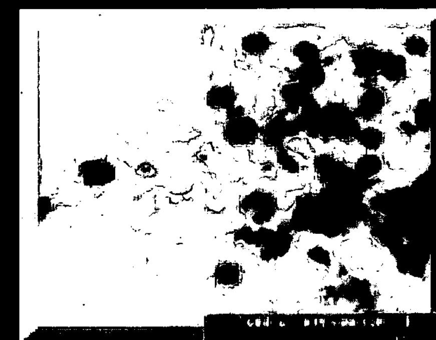
Pt/carbon black catalyst

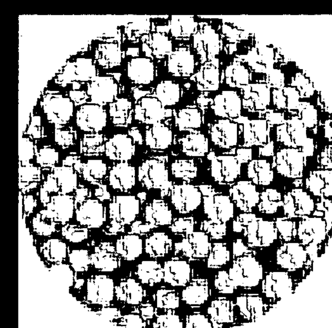


Heart of a Packed Bed Reactor



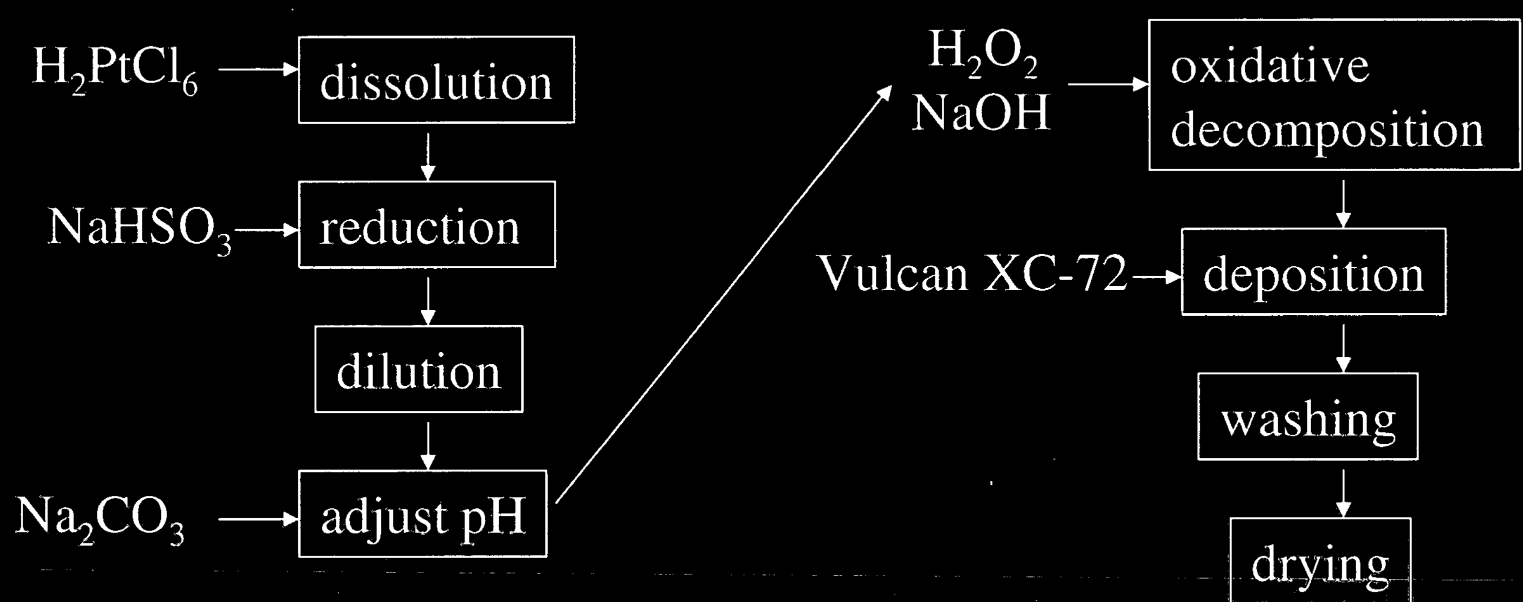






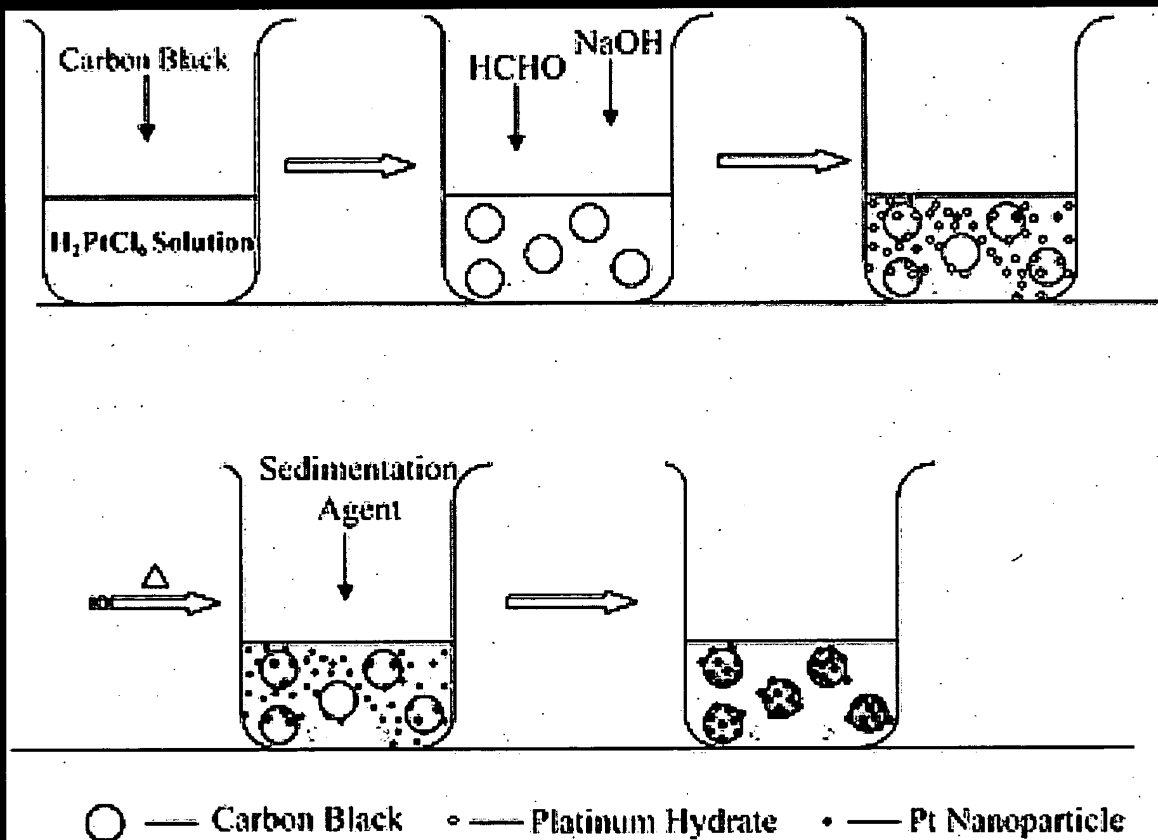
Motivation

- Prevalent methods for producing fuel cell electrodes are often cumbersome (e.g. E-TEK, Watanabe et al., J. Electroanal. Chem. 229 (1987) 395)



- We've applied our fundamental insights on electrostatic adsorption to carbon materials, so as to greatly simplify the process

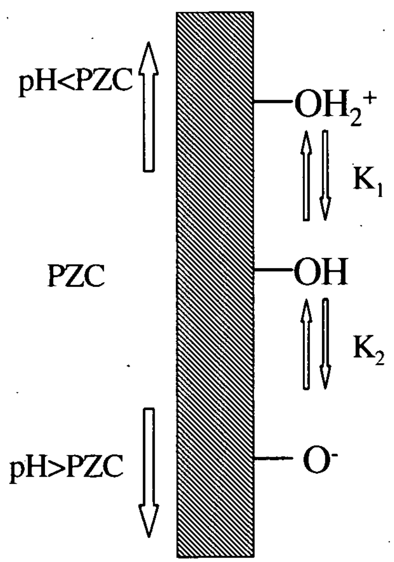
Zhou, Zhenhua et al. (Qin Xin), Phys. Chem. Chem. Phys. 2003, 5(24), 5485-5488.



1) Suspend in CPA
2) Add formaldehyde
3) Gradually add NaOH to pH 14
4) Age
5) Heat
6) Sediment with strong electrolyte
7) Filter and wash
8) Dry in vacuum

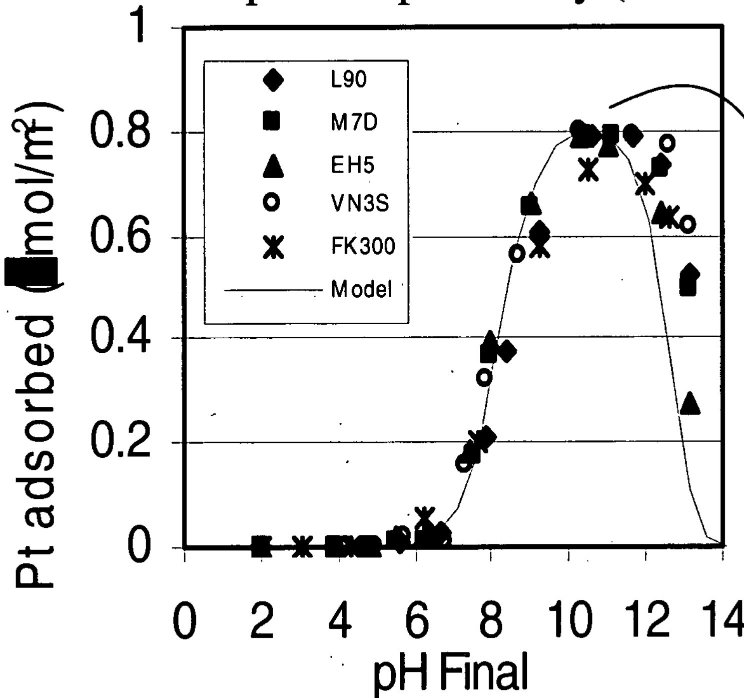
Method of "Strong Electrostatic Adsorption (SEA)"

Electrostatic mechanism

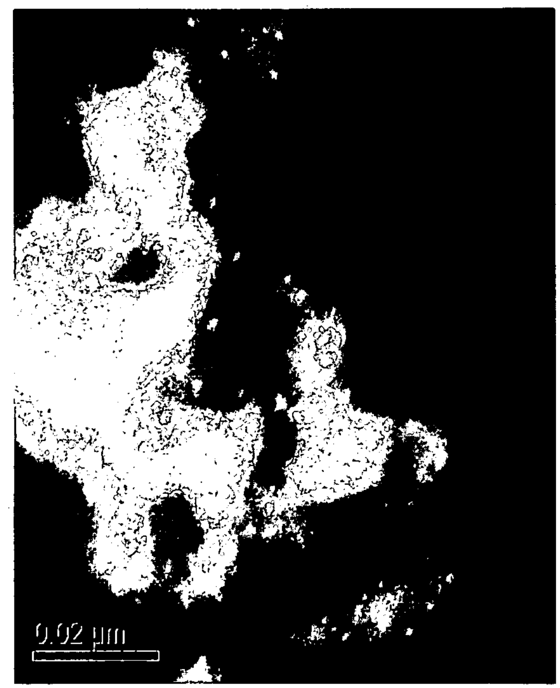


$[(NH_3)_4Pt]^{+2}$

Pt uptake – pH survey (Schreier & Regalbuto, J. Cat. 2004)



H_2

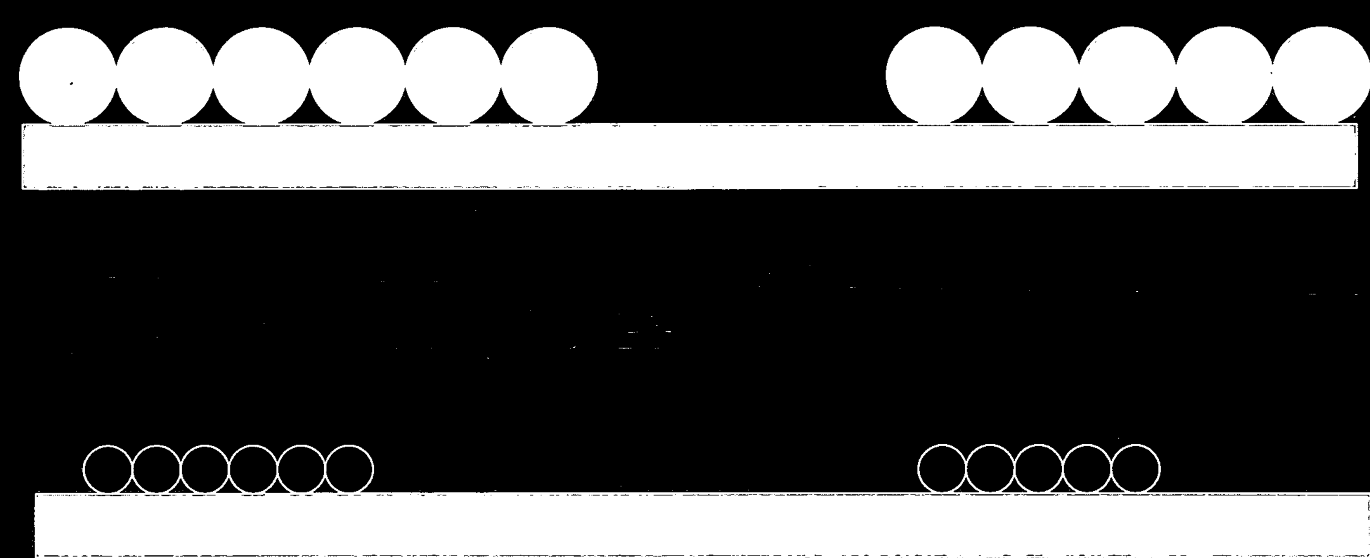


Reduction to preserve dispersion

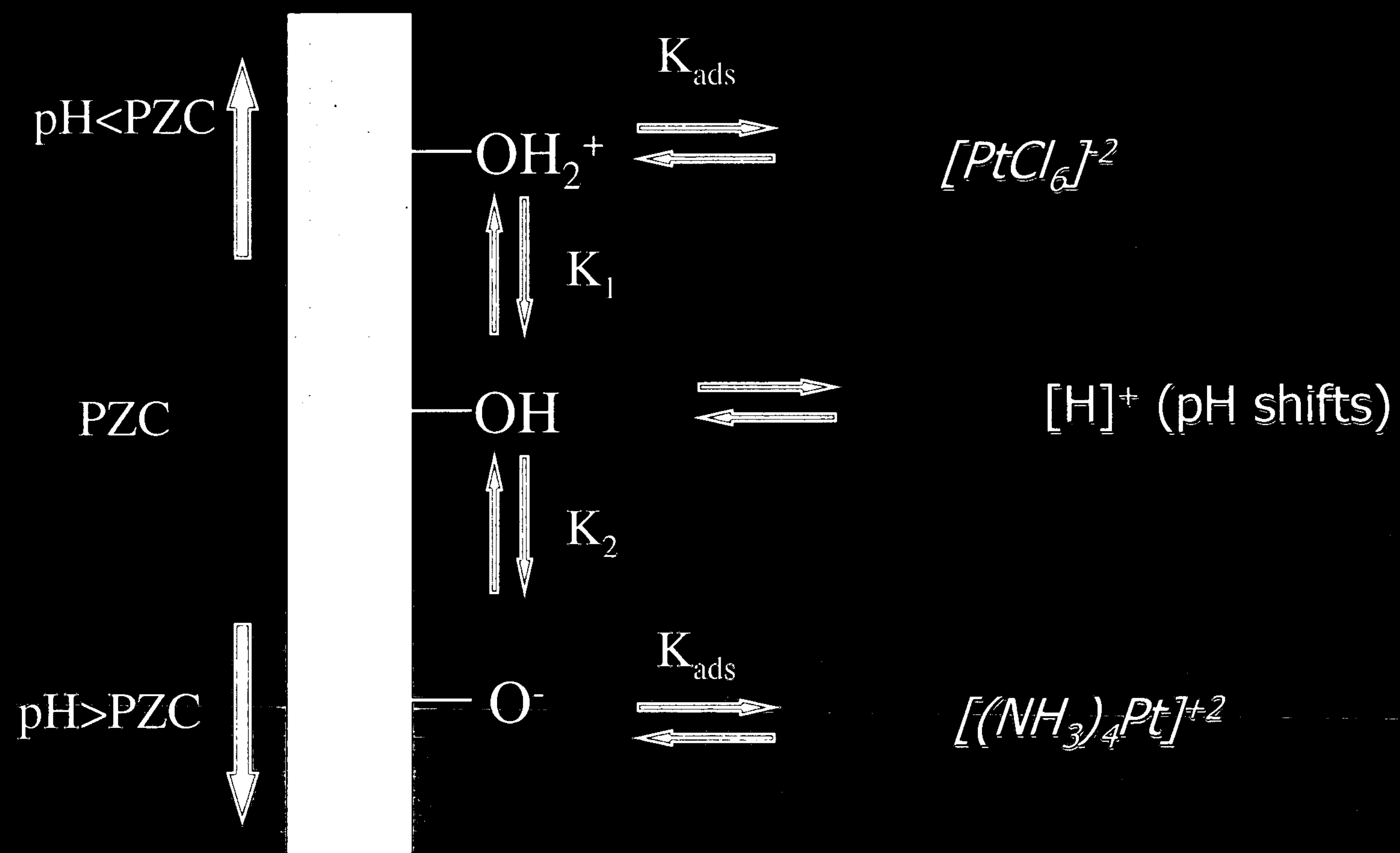
Motivation

- Prevalent methods for producing fuel cell electrodes are often cumbersome (e.g. E-TEK, Watanabe et al., J. Electroanal. Chem. 229 (1987) 395), use Pt sulfite acid

- Hypothesis: SEA of common Pt precursors will lead to high dispersion of reduced (finished) catalyst:

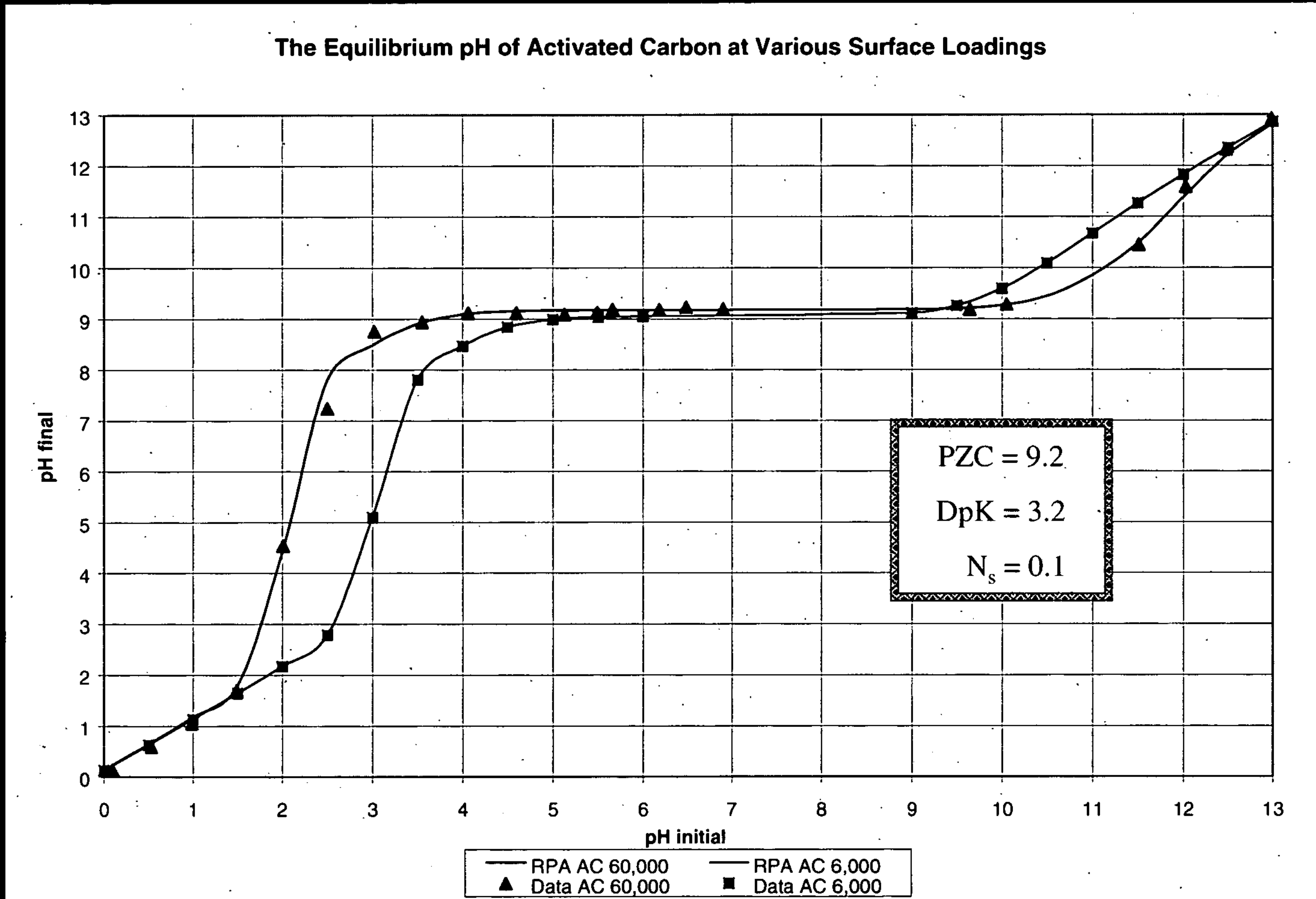


RPA Model Components



Carbon PZC results

(Melanie Timmons and Teresa Feltes, NSF REU)



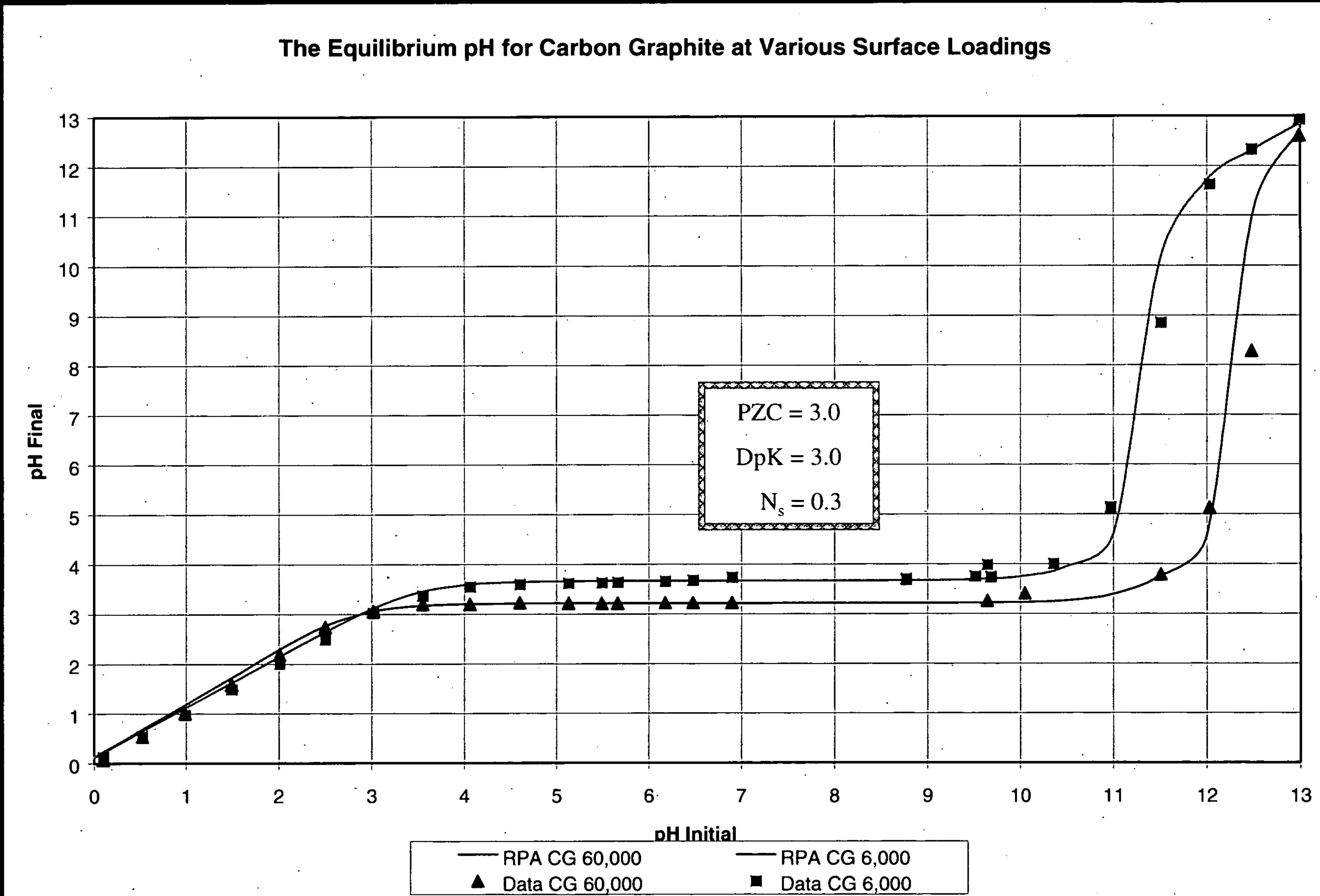
Surface Loading

2000 m^2/l

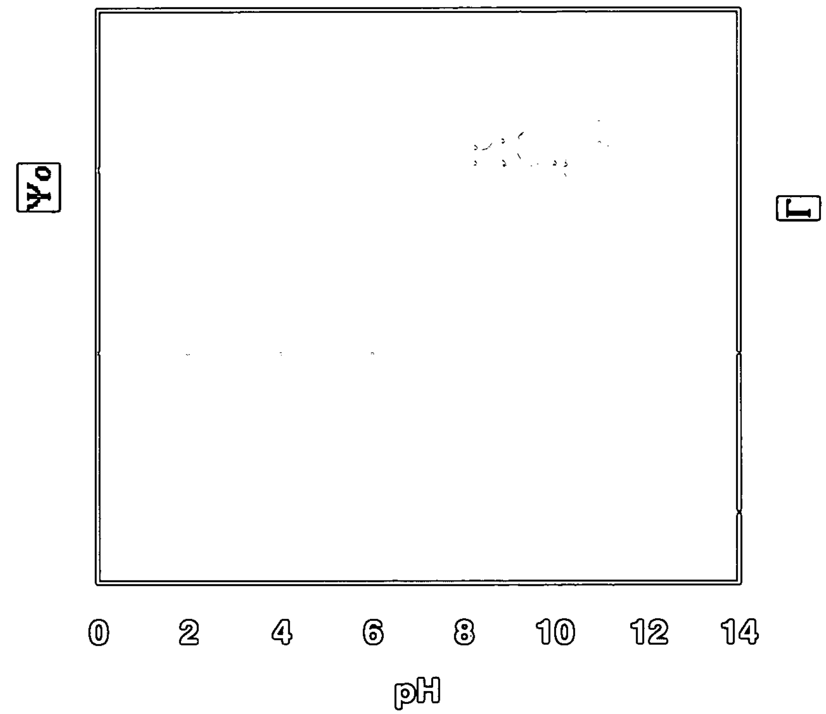
200,000 m^2/l

- the solid surface has a dramatic effect on solution pH (Park and Regalbuto, JCIS 1995)

Carbon PZC results



Revised Physical Adsorption (RPA) Model



System Parameters:

initial concentration C [mol/l]
surface loading SL [m^2/l]
temperature T [K]
final pH

Precursor Parameters:

radius of hydrated ion r_i [m]
valence z [-]
number of hydration sheaths

Support Parameters:

point of zero charge PZC [-]
surface ionization constants ΔpK [-]
dielectric constant of the oxide ε [-]
hydroxyl site density N_s [1/nm^2]

Fundamental Constants:

e, ε_0, k, F, N_0, r_w, R, ε_w

$$\theta = \frac{\Gamma}{\Gamma_{max}} = \frac{K_{Pt} C_{Pt}}{1 + K_{Pt} C_{Pt}}$$

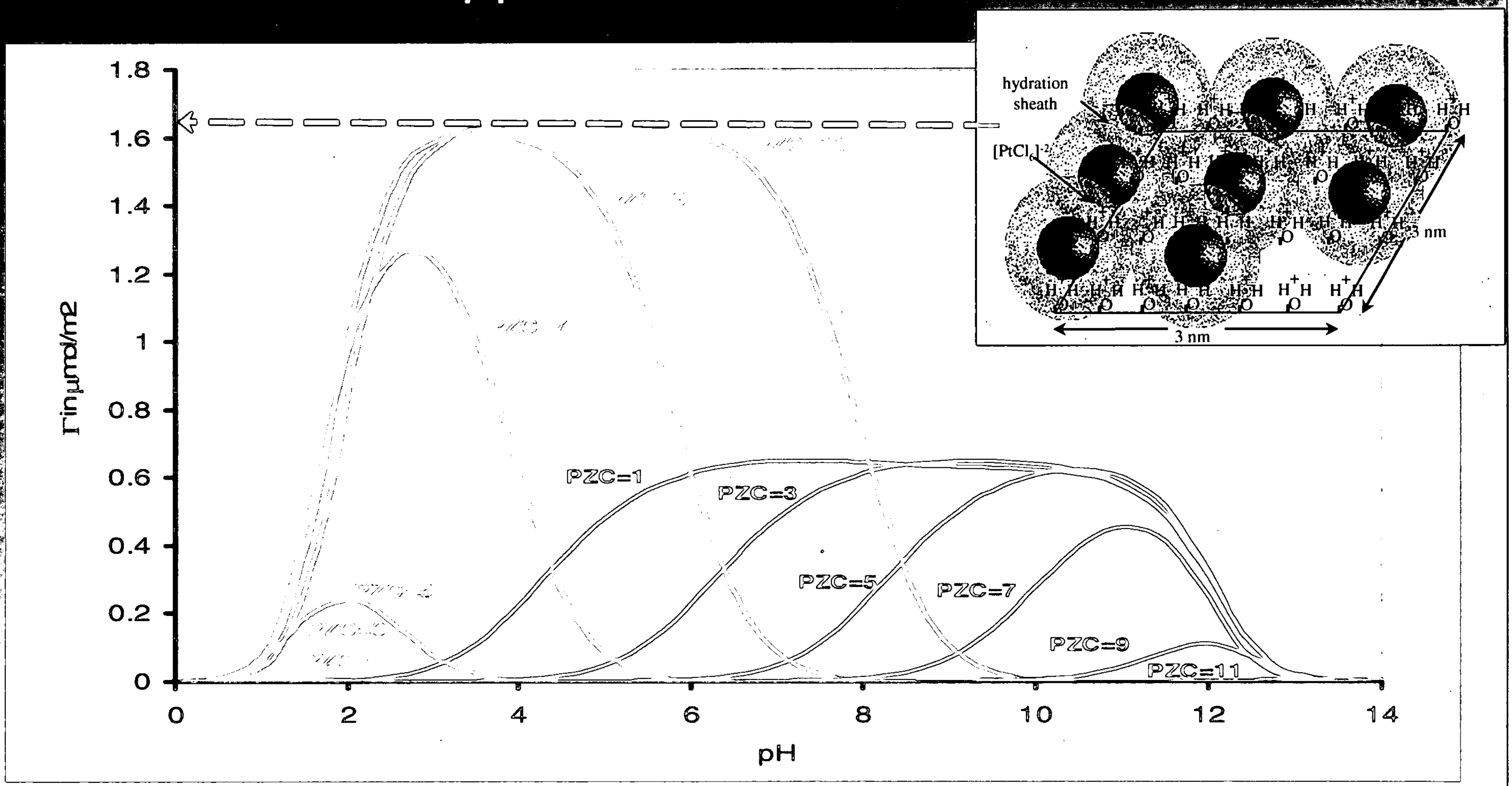
$$-RT \ln K_i = \Delta G_{coul,i}$$

$$\Delta G_{coul,i} = z_i F \psi_{i,x}$$

$$\psi_{i,x} = \left(\frac{2RT}{zF}\right) \ln\left(\frac{(Y+1) + (Y-1)\exp(-\kappa x_i)}{(Y+1) - (Y-1)\exp(-\kappa x_i)}\right)$$

$$Y = \exp\left(\frac{zF\psi_0}{2RT}\right)$$

RPA Simulation of CPA and PTA Adsorption Over Supports with Different PZC



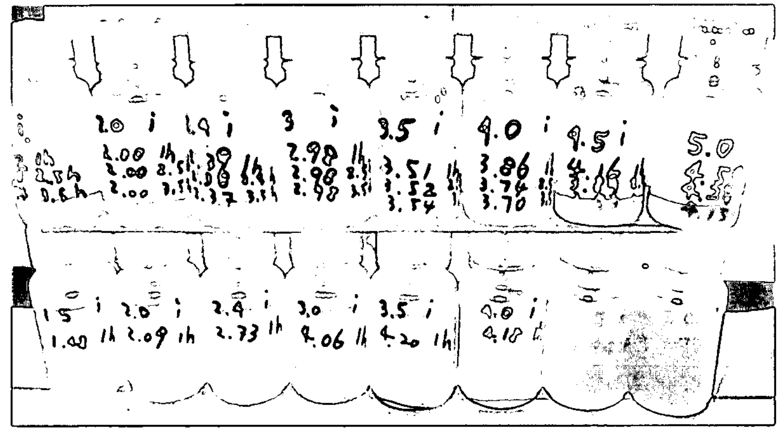
CPA H_2PtCl_6 PTA $(NH_3)_4PtCl_2$

Methods

ICP for measurement of [Pt], [Al] /ppm

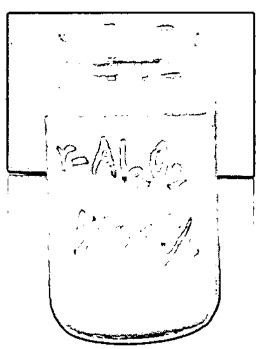
Surface coverage = μmol/m^2 =

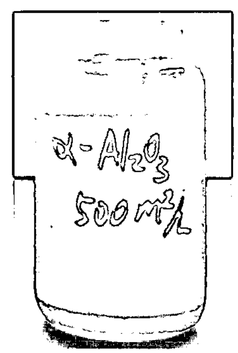
$(C_{Pt,\ initial} - C_{Pt,\ final})/SL$



SL = Surface Loading:

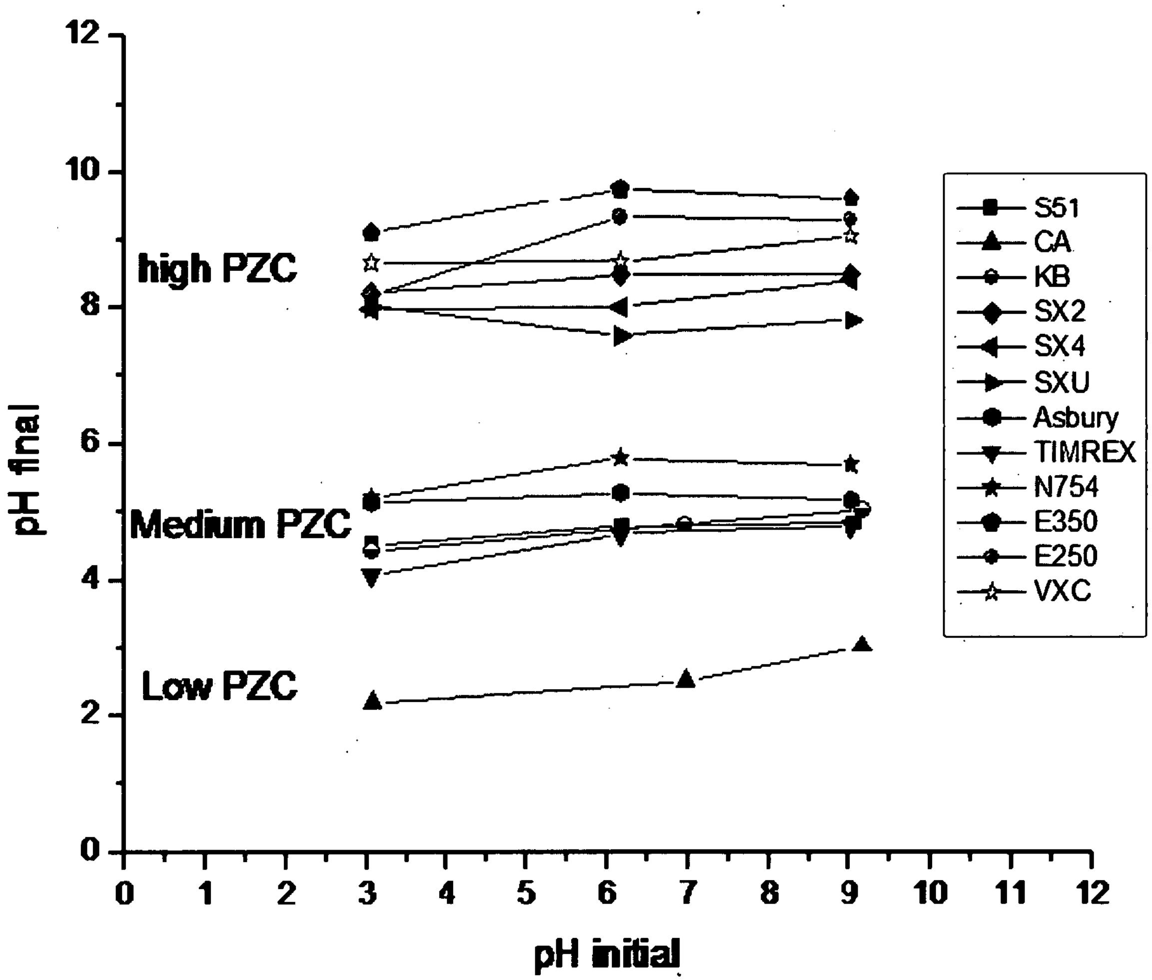
$$\frac{0.0903\ g\ \gamma\text{-}Al_2O_3\ (277\ m^2/g)}{0.050L} = \frac{1.786\ g\ \alpha\text{-}Al_2O_3\ (14\ m^2/g)}{0.050L} = 500 m^2/L$$



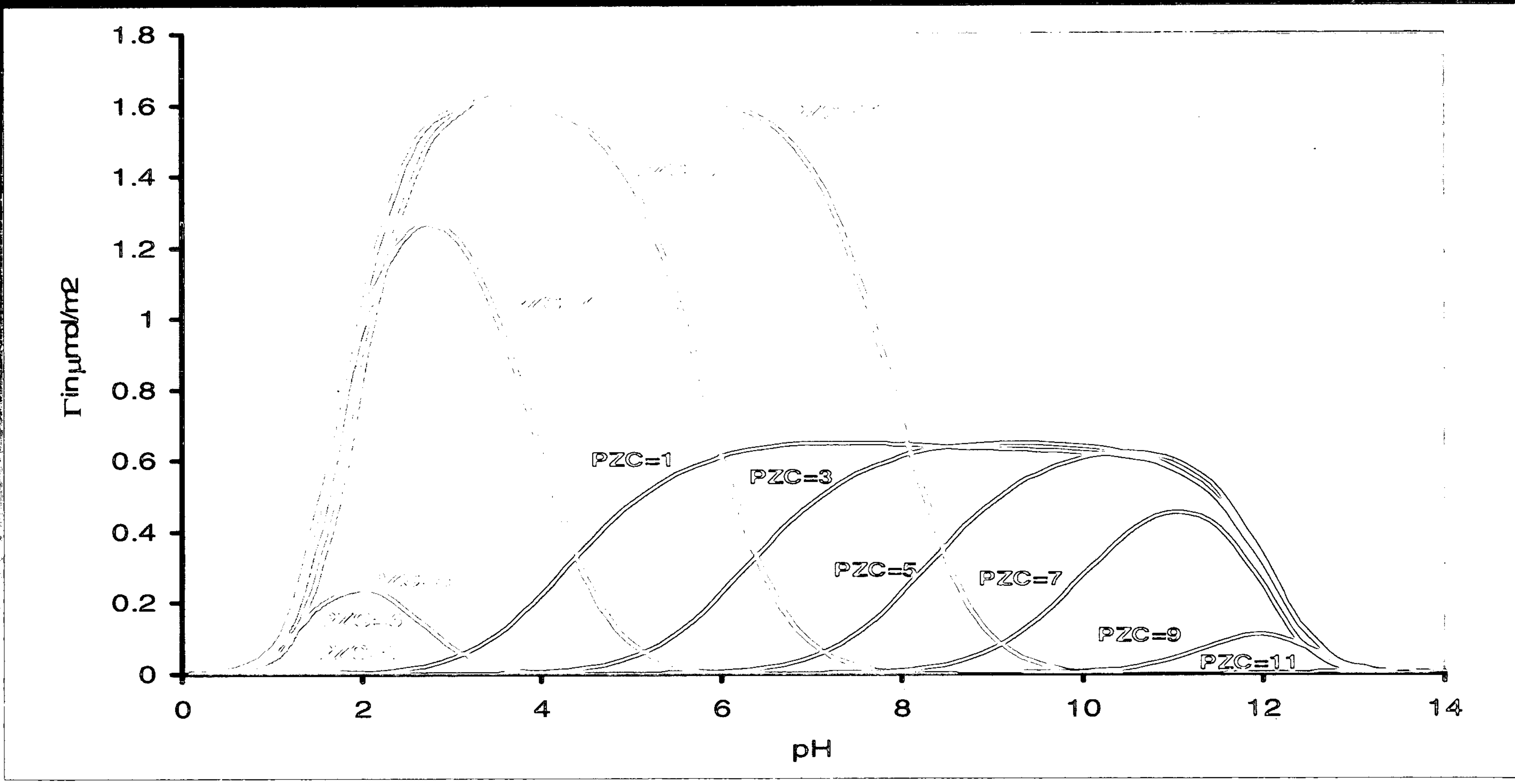


Carbon Name	Abbrevi-ation	SA (m^2/g)	Pretreatment	Total Pore Volume (ml/g)	PZC
Activated carbon					
Darco s-51	S51	650	Acid washed, steam activation of lignite coal	1.0	4.7
Norit SX 2	SX2	800	Acid washed steam activated	1.36	8.4
Norit SX 4	SX4	650	Acid washed steam activated		7.9
Norit SX ULTRA	SXU	1200	Acid washed steam activated	2.16	7.8
Norit CA-1	CA	1400	Chemically activated by phosphoric acid	0.9	2.6
Darco KB-B	KB	1500	chemical activation of hardwood	1.8	4.8
Graphite					
Asbury Grade 4827	ASBURY	115	Heated, ground natural graphite	2.55	5.2
Timcal TIMREX HSAG 300	TIMREX	280	Heated, ground petroleum coke	1.64	4.5
Carbon Black					
Degussa A1-04088 N754	N754	25	pyrolysis	0.7	5.6
Ensaco 250 Powder	E250	62	pyrolysis	1.4	9.0
Ensaco 350 Powder	E350	770	pyrolysis	8.0	9.5
Vulcan XC 72	VXC	254	pyrolysis	3.46	8.9

PZC Determinations of Carbons



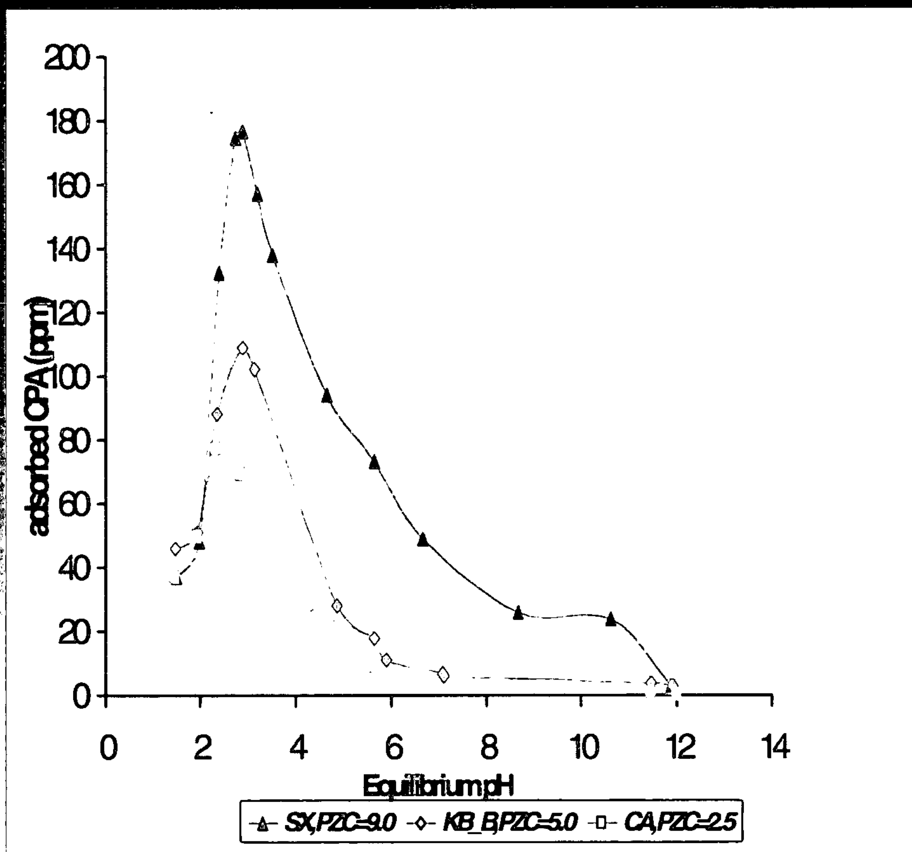
RPA Simulation of CPA and PTA Adsorption Over Supports with Different PZC

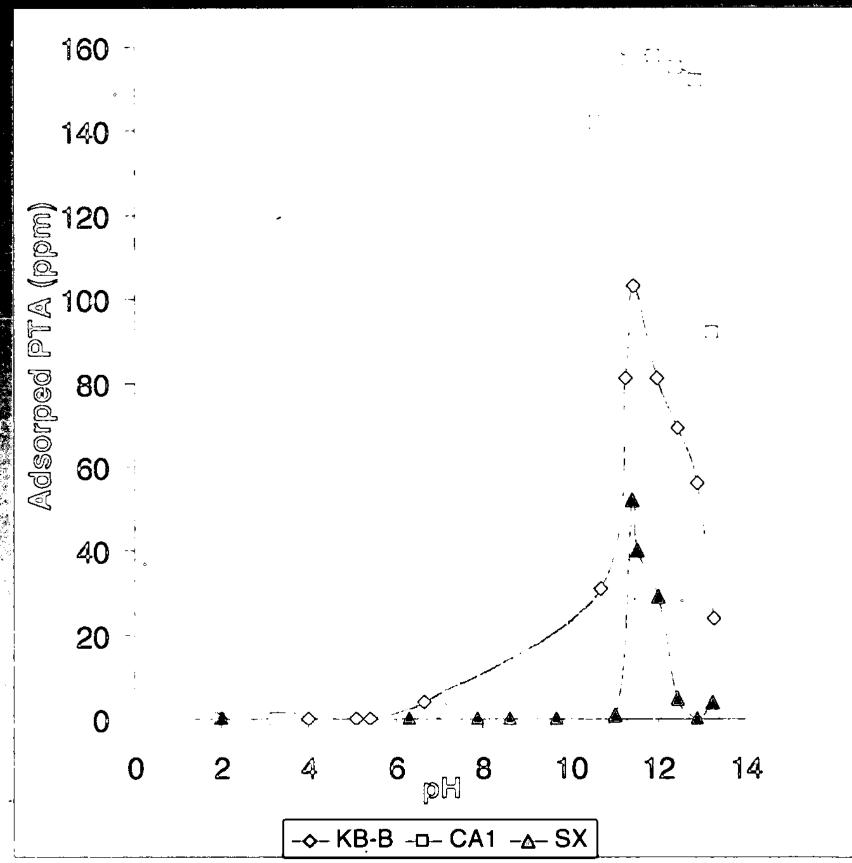


CPA H_2PtCl_6 PTA $(NH_3)_4PtCl_2$

CPA, PTA uptake vs. pH, varying PZC

$[PtCl_6]^{-2}$ (activated carbon) $[(NH_3)_4Pt]^{+2}$

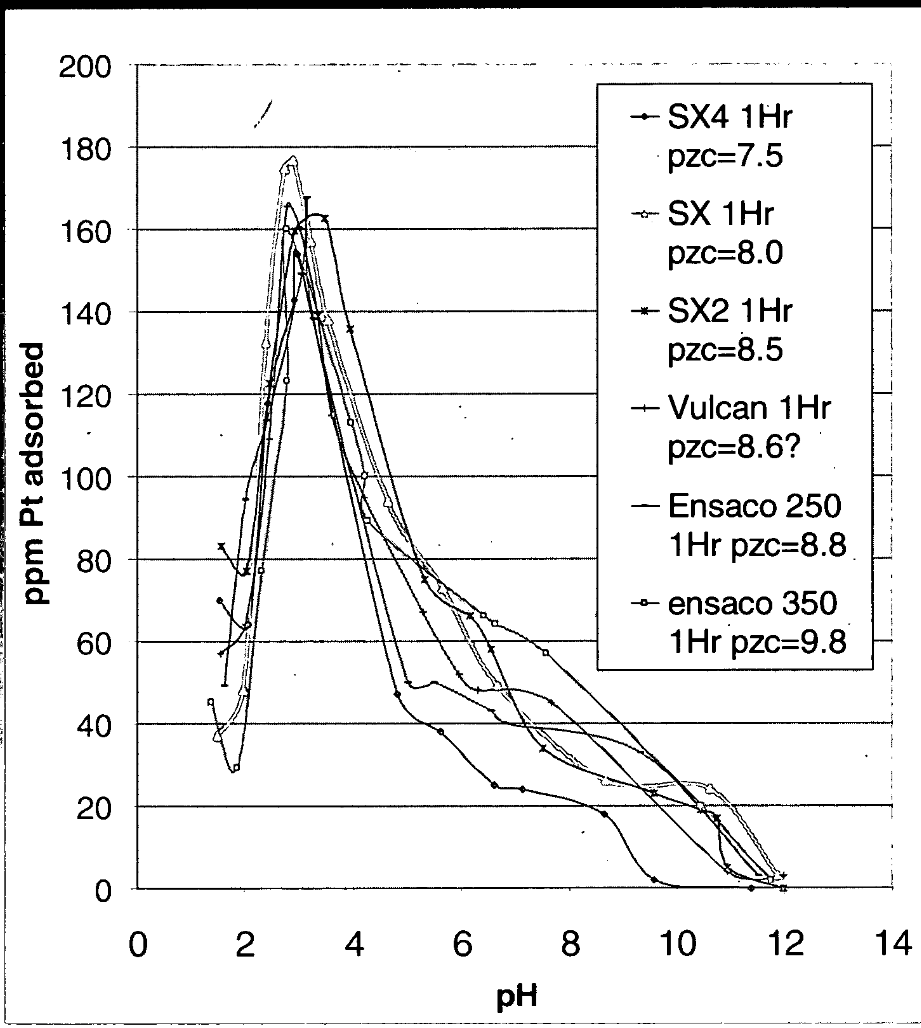




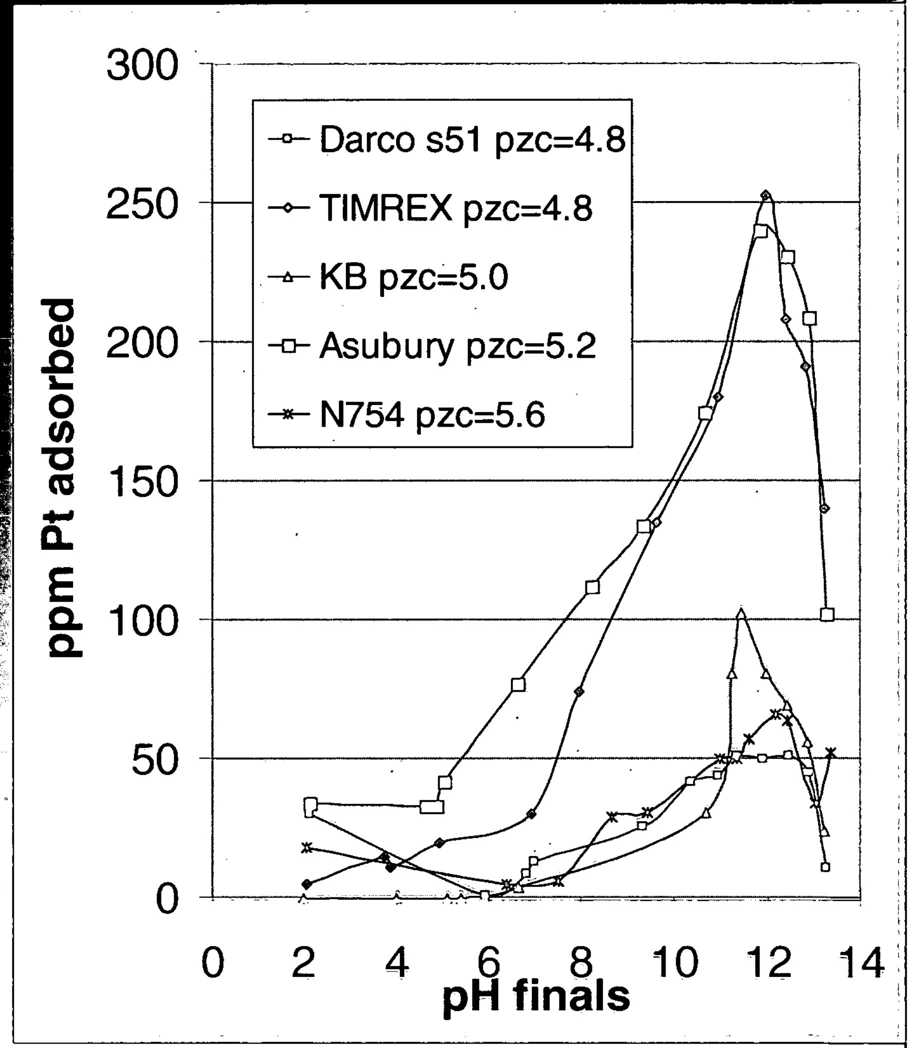
Xao and Regalbuto, J. Mol. Catal. 219, 2004, 97.

CPA, PTA uptake vs. pH, varying carbon type

CPA/high PZC

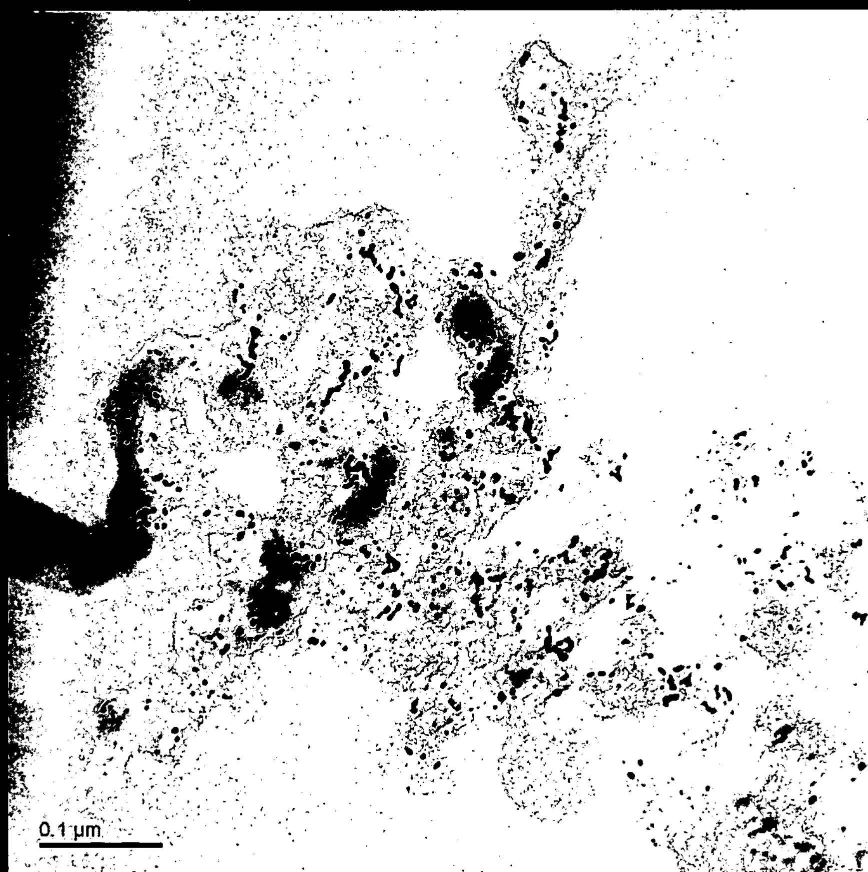


PTA/mid PZC

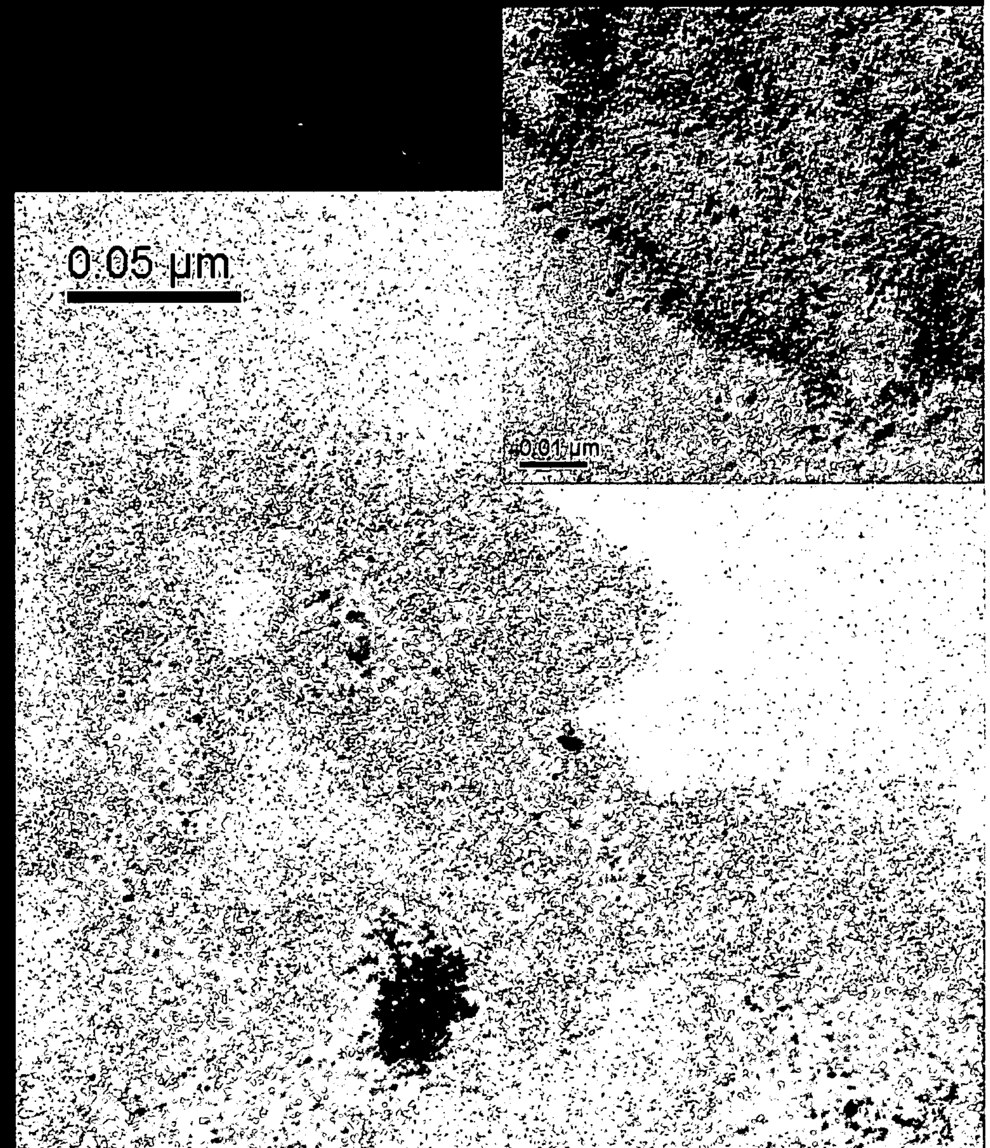


- narrower volcano curves w.r.t alumina, silica
- pore exclusion of PTA from small pore carbons at high pH

STEM of PTA/Timrex after 200°C Reduction



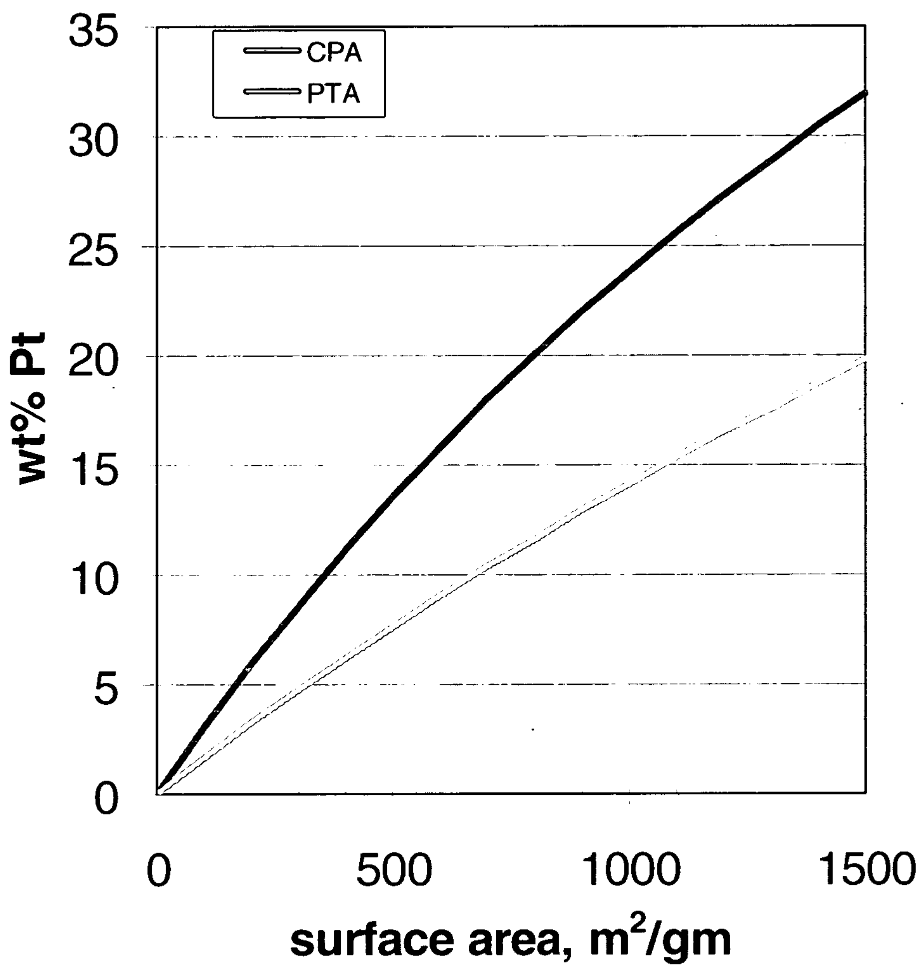
- average size ≅ 8-10 nm



- average size ≅ 1-2 nm

Fuel Cell Electrocatalyst Synthesis

Max. loading via SEA

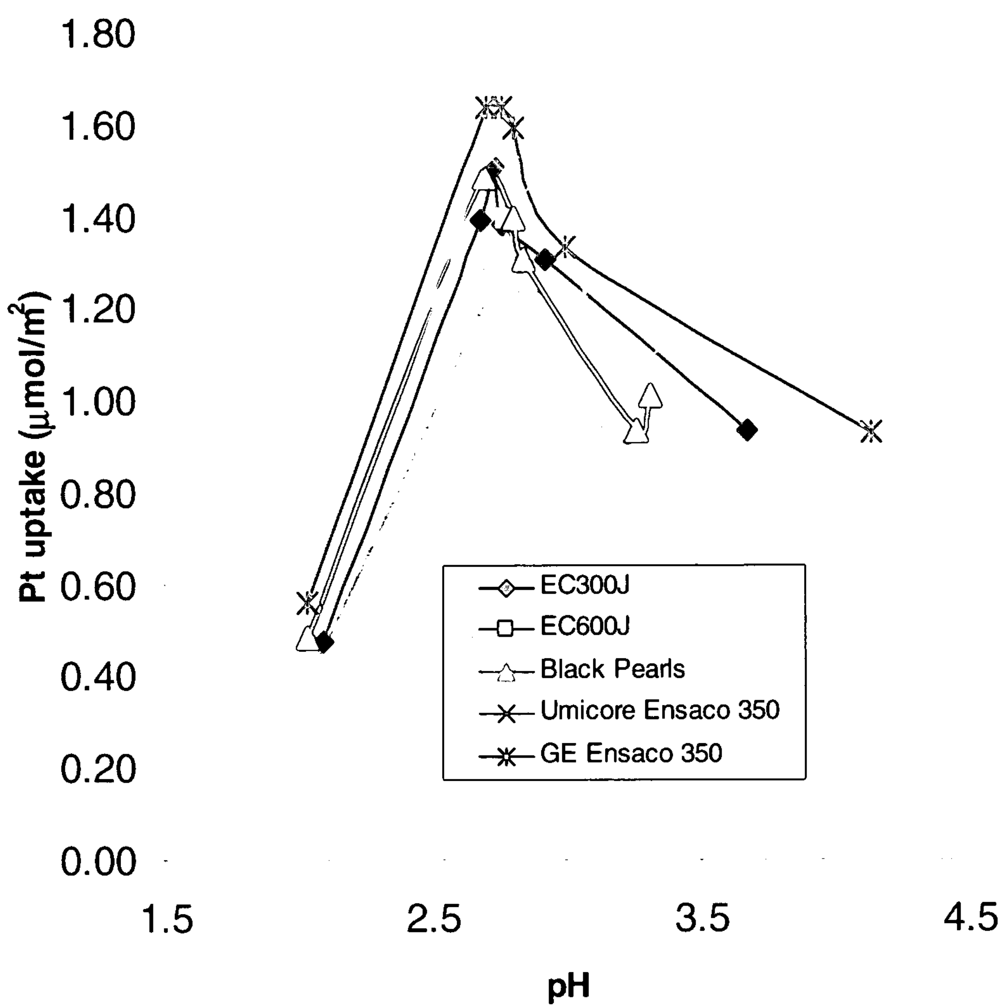


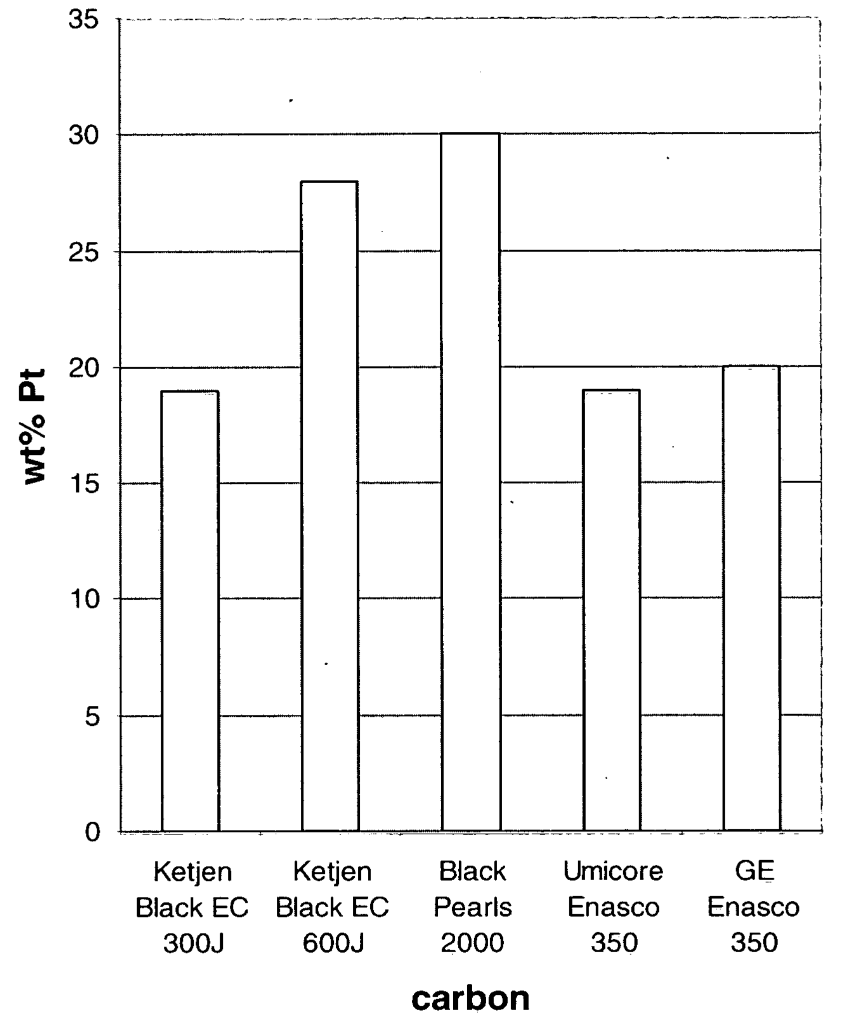
Carbon Black	Surface area (m^2/g)
Ketjen Black EC 300J	795
Ketjen Black EC 600J	1415
Black Pearls 2000	1475
Enasco 350	795

- CPA limit: 1.6 $\mu mol/m^2$
- PTA limit: 0.84 $\mu mol/m^2$

(Santhanam et al., Catal Today 1994)

CPA uptake vs. pH, carbon blacks

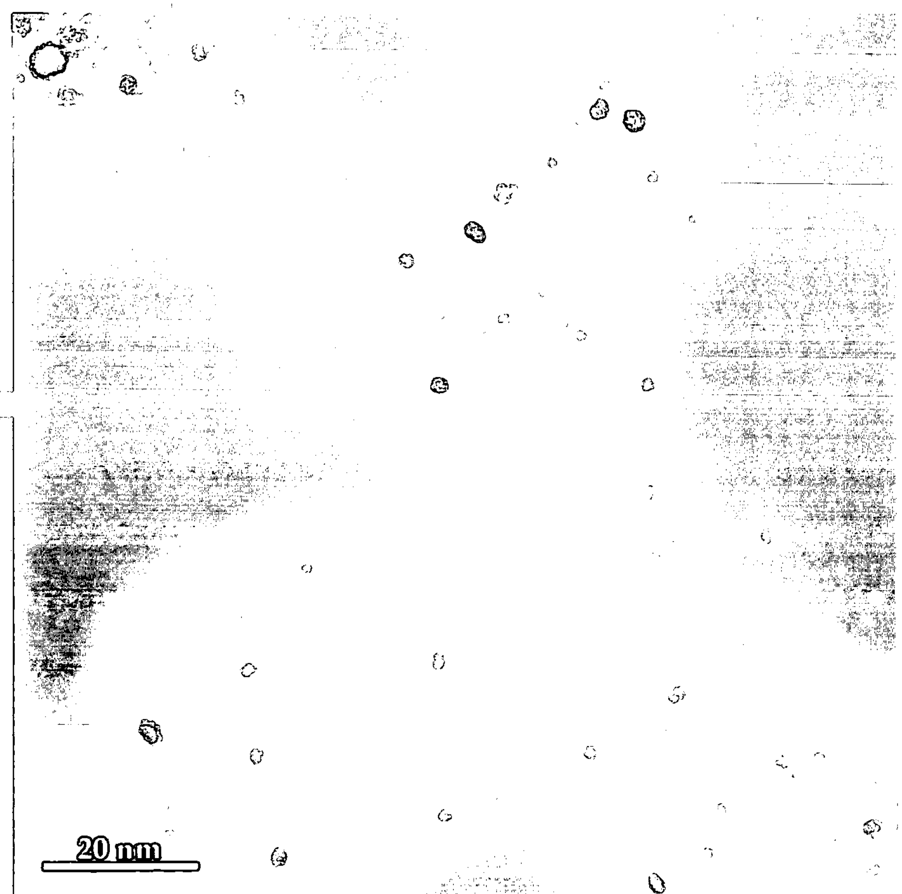




- optimal pH = 2.9
- max loading achieved = 30 wt% Pt

Comparison of Platinum Particle size on High Surface Area Carbon Black (BP2000, 1500 m^2/gm)

SEA, 500 m^2/l, pH 2.9, 200°C reduc.



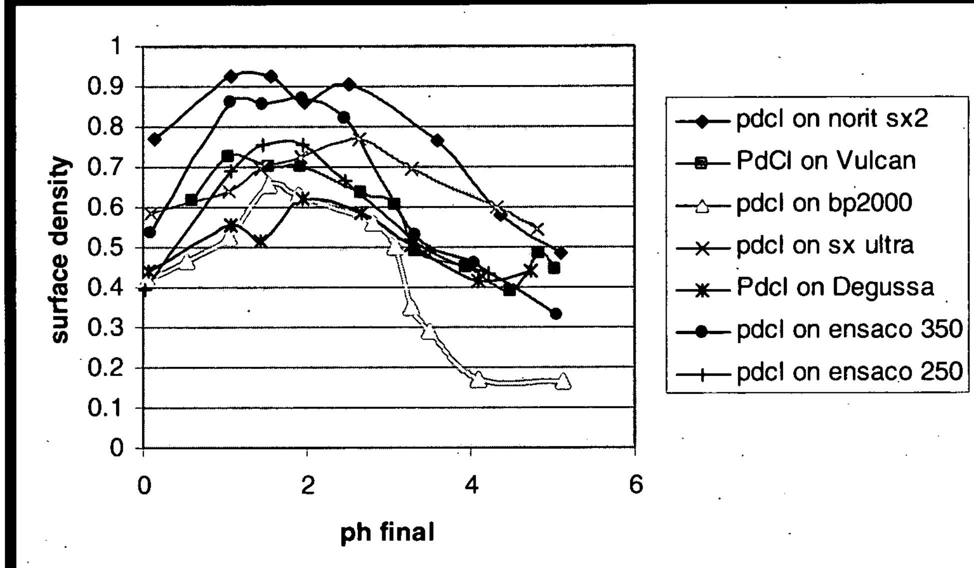
o Good dispersion and small particle size (1-2 nm)

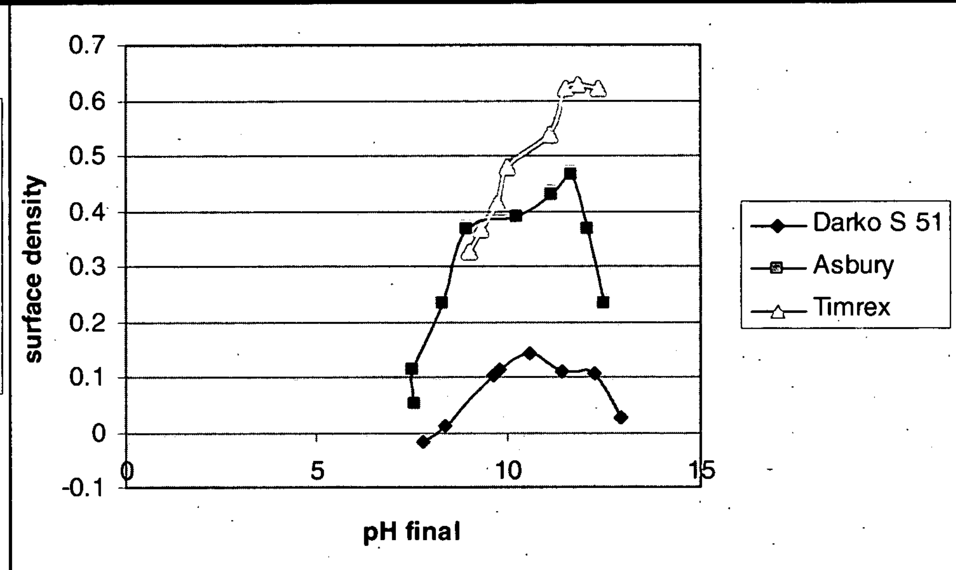
Pt utilization in high SA carbon blacks

sample	SA m^2/gm	wt % Pt	Pt area (m^2 Pt/gm Pt) SEA at pH 2.9
Ketjen 300	800	19	93 (91)*
Ketjen 600	1415	28	62
BP 2000	1475	30	116
Ensaco 350	795	19	112

* measured independently by H. Gasteiger, GM, with cyclic voltammetry

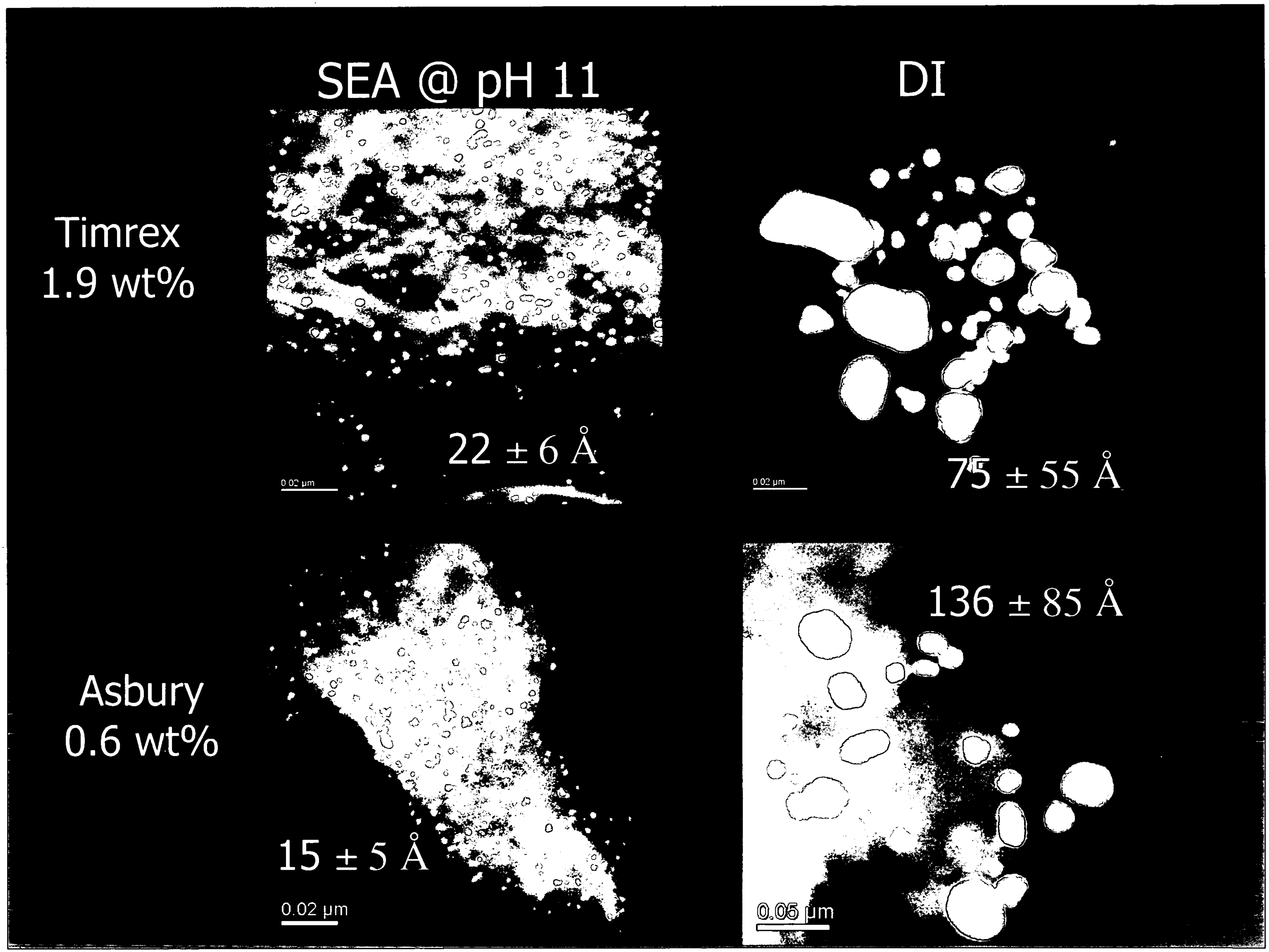
Pd(II) uptake on carbon

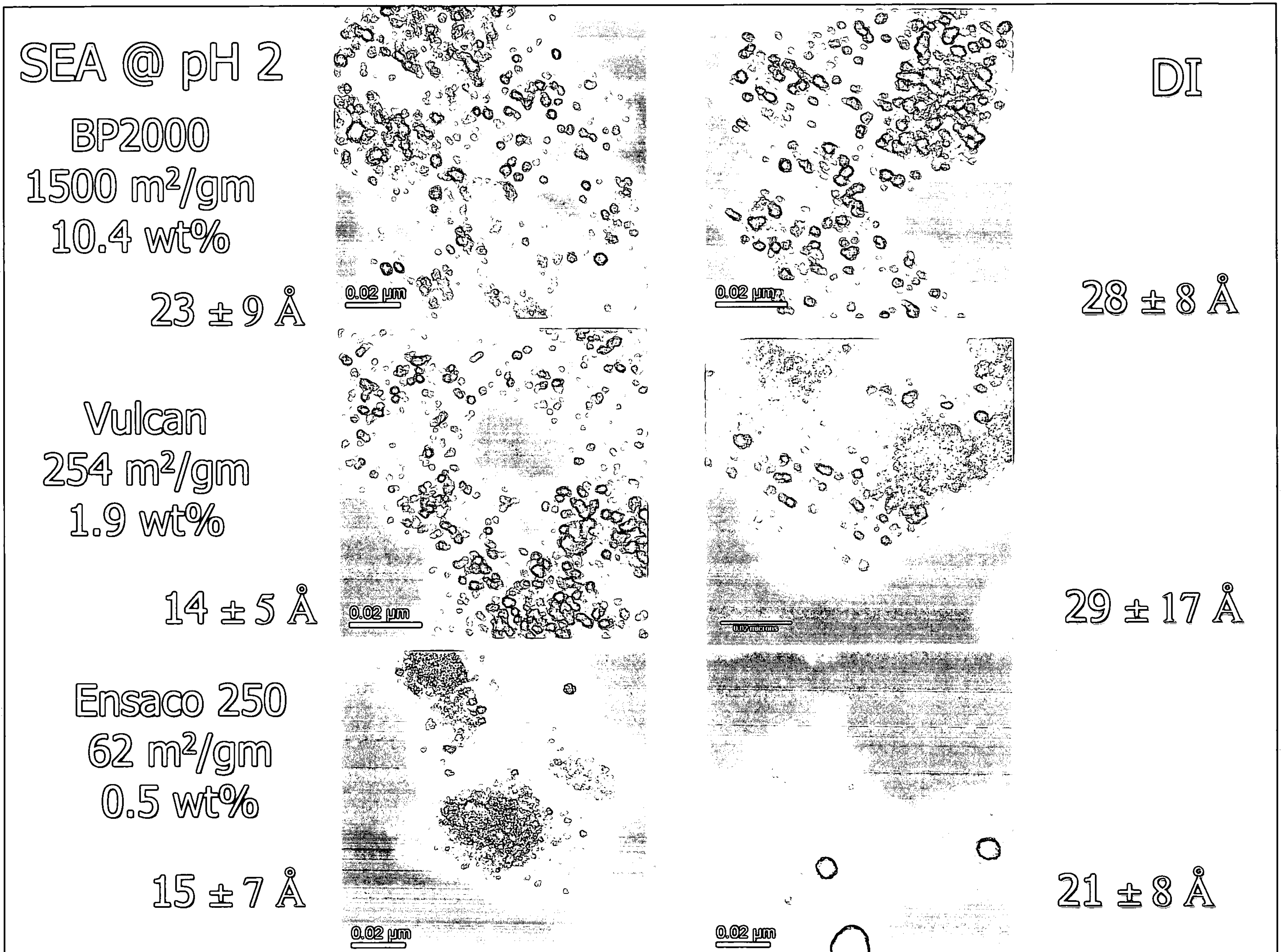




$[PdCl_4]^{-2}$ dissolved in 5.6 times excess Cl; basified with NH_4OH

$[(NH_3)_4Pd]^{+2}$ starting solution, basified with NaOH


SEA @ pH 11
DI
Timrex
1.9 wt%
22 ± 6 Å
0.02 µm
75 ± 55 Å
0.02 µm
Asbury
0.6 wt%
15 ± 5 Å
0.02 µm
136 ± 85 Å
0.05 µm


SEA @ pH 2
BP2000
1500 m²/gm
10.4 wt%
23 ± 9 Å
Vulcan
254 m²/gm
1.9 wt%
14 ± 5 Å
Ensaco 250
62 m²/gm
0.5 wt%
15 ± 7 Å
DI
28 ± 8 Å
29 ± 17 Å
21 ± 8 Å
0.02 μm
0.02 μm
0.02 μm
0.02 μm
0.02 μm
0.02 microns

JR vs. Ebner

- Objective:
  - Ebner: deposit NM on oxygen free carbon to reduce leaching, sintering
  - JR: deposit highly dispersed NM on either O-free of O-containing carbon

Mechanism:
  - Ebner: reactive deposition by hydrolysis of NM complex at high pH
  - JR: electrostatic deposition at optimal pH at either pH range

JR vs. Fischer

- Objective:
  - Fischer: deposit NM on metal substrates (including carbon steel)
  - JR: deposit highly dispersed NM on any type of carbon
- Mechanism:
  - Fischer: electroless deposition at high pH by reduction of NM complex, always have one reducing agent in solution
  - JR: electrostatic deposition at optimal pH at either pH range, no reducing agent in solution

Conclusions

- SEA is a good, simple method for the synthesis of Pt/C materials with common Pt complexes
  - CPA: use PZC ~ 9 carbon, pH ~2.9
  - PdTC: use PZC ~ 9 carbon, pH ~2-3
  - PTA, PdTA: use PZC ~ 4-5 carbon, pH ~10.5
  - PTA/high pH; steric exclusions for high SA carbons
- SEA method is based on a simple electrostatic mechanism of monolayer adsorption of charged metal complexes
- SEA method does not involve hydrolyzing or reducing agents